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Corrosion studies on copper

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Corrosion on copper was caused by keeping a copper wire in a silver nitrate solution for a known time. The variation in electrical resistance with volume as a result of corrosion is correlated with the Grüneisen parameter indicating the systematic corrosion process. The study of the reduction in the mass of the sample as a function of corroding time in different concentrations of silver nitrate solution has thrown light on a parameter (τ) called the *effective corrosion time* that is characteristic of the copper-silvernitrate solution system

1. INTRODUCTION

The growth of silver fibres from solution has been reported (Sake Gowda & Madaiah 1968) by keeping the copper wire in silver nitrate solution The substitution of silver for copper was found to be the reaction that was favourable to the surface nucleation The radial growth of fibres was faster in higher concentrations of $AgNO_3$ solution Early X-ray investigations have shown that these fibres are purely silver It was of interest to consider this electrolytic action as the basis for corrosion and hence to study the effects on the electrical behaviour of copper that is commonly used as conducting material So in the present work, the corrosion of copper surface was studied using silver nitrate solution of different concentrations at room temperature The copper wire was kept in a long cylinder containing silver nitrate solution for a known interval of time and it was observed that the surface was uniformly affected all around. The reduction in the thickness of the wire was found to depend on the concentration of the silver nitrate solution The electrical resistance of the copper wire was measured before and after corrosion using Kelvin's bridge method The measurements revealed the systematic variation in the resistance as a function of concentration of the solution as long as the time of corrosion was maintained the same These measurements have been correlated with the Gruneisen's parameter which has greater significance in the vibrational spectrum of a solid with the volume variation The effective corrosion time has been determined by the study of the loss in mass of the copper sample due to the reaction as a function of corrosion time and using different concentrations of silver nitrate solution. The *Corrosion time parameter* for the copper-silver nitrate solution system was found to be independent of the concentration of corroding solution and this parameter seemed to be a very significant one characteristic of the system.

2. Experimental Procedure

(a) *Preparation of corroded copper wires* :

A copper wire of known length (60 cms) and thickness) 0·1 cms) was kept in a silver nitrate solution of known concentration in a long cylinder. The reaction was allowed to take place for a known interval of time and the surface of copper was thus allowed to be affected by the corrosion process which is basically electrolytic. After a known corrosion time the copper wire was removed from the solution and the surface cleaned with distilled water. Thus the corroded sample of wire was prepared. Samples were prepared by varying the concentration of silver nitrate solution keeping the time of corrosion constant.

(b) *Measurements*

The electrical resistance of corroded samples of copper was measured by using Kelvin's double bridge correct to 10^{-5} ohms. The measurement was also done before corroding the samples. The fractional change in resistance ($\Delta R/R$) was determined as a function of the concentration of the corroding solution. The results are shown in figure 1.

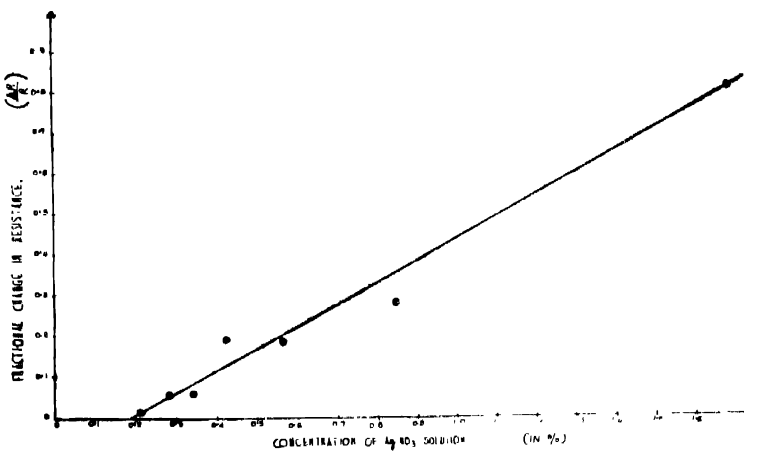

Fig. 1

The fractional change in linear density of the samples was also determined as a function of the concentration of the corroding solution, and the results are shown in figure 2.

The change in electrical resistance of corroded copper wire for a given concentration of silver nitrate solution was found to be linear with the change in linear density provided the corrosion time was the same. This could be seen

in figure 3, where the fractional change in resistance is shown as a function of fractional change in linear density of the wire.

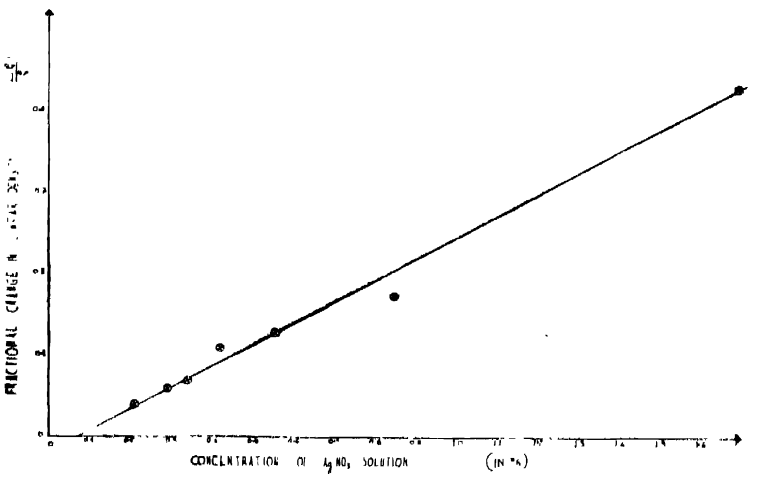

Fig. 2

The mass of copper wire before and after corrosion was measured for a given concentration of silver nitrate solution as a function of time. At regular intervals of 24 hours the mass of the sample was determined. This was done using different samples of the same material with the same dimensions. These observations

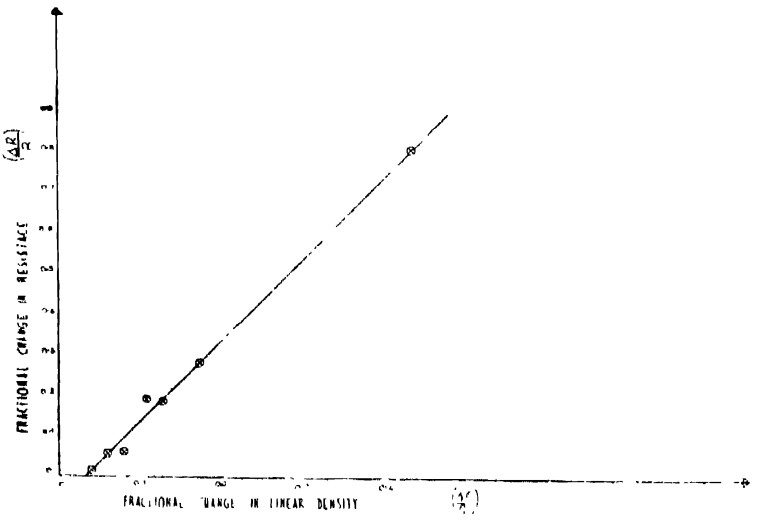

Fig. 3

were repeated for other concentrations of silver nitrate solution. The results are shown in figure 4.

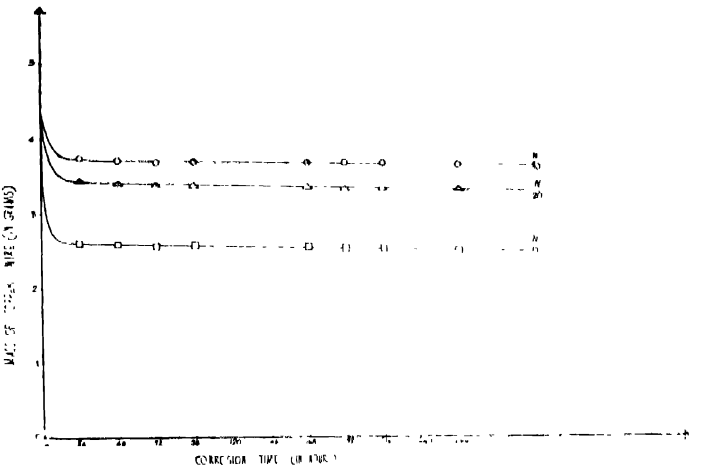

Fig. 4

3. Results and Discussion

The corrosion of copper was caused by keeping the copper wire in silver nitrate solution, the process of which could be understood as follows. Since the position in the electromotive force series (Richards 1965) is earlier to silver the copper ions dissolve more easily in the electrolyte and the silver atoms get reduced and replace copper ions. This substitution reaction gives rise to the silver fibres. The reaction can be represented as $Cu \rightarrow Cu^{++} + 2e$; $2e + 2Ag^{+} \rightarrow 2Ag$. The first equation indicates the change from metallic copper to copper ions in solution, leaving two electrons behind. The second represents the change from silver ions in solution to metallic silver through the two electrons. The silver is therefore deposited on the copper surface resulting in the growth of silver fibres. The eating away of the copper surface is seen thus basically due to electrolytic reaction. The microscopic differences from point to point in the surface of the copper are due to differences in composition of individual metal grains, different crystal orientation and the grain boundaries themselves. The grain boundary corrosion is mainly important because of energy considerations. The grain boundaries are at a higher energy level than the atoms within the grains, those in the grain boundaries tend to dissolve more easily so that these areas become anodic. They are therefore eaten away more rapidly by corrosion.

The results of the experiment reveal that the variation of the fractional change in electrical resistance and in the linear density of the corroded samples for a known corrosion time are found to be linear with the concentration of the

corroding solution. This enables us to correlate the changes in electrical resistance with the changes in volume and thus to link with the Grüneisen parameter which relates the vibrational spectrum with the volume changes as clear from the following argument. We know that the electrical resistance (R) of a conductor is related to the length and area of cross-section (a) by the equation.

$$R = \sigma \frac{l}{a},$$

where σ is the resistivity of the material. In the present case the length of the sample was maintained constant and therefore the fractional change in resistance is given by

$$\frac{\Delta R}{R} = - \frac{\Delta a}{a}.$$

Since the fractional change in area of cross section is the same as the fractional change in volume (V) we write

$$\frac{\Delta R}{R} = - \frac{\Delta a}{a} = - \frac{\Delta V}{V},$$

or

$$- \left(\frac{\Delta R}{R} \right) \left(\frac{V}{\Delta V} \right) = - \frac{d \ln R}{d \ln V} = \text{constant}$$

as observed.

Further, for a given length of the sample the resistivity change depend on the product Ra. So the Grüneisen's parameter (γ) which is equal to $- \frac{d \ln \sigma}{d \ln V}$ (MacDonald 1964) and thus becomes as $\gamma = - \frac{d \ln Ra}{d \ln V}$. This argument shows in a convincing way the relevance of γ. Since the observations indicate that $- \frac{d \ln R}{d \ln V}$ = constant, it confirms in a way that the corrosion in this case as very systematic and regular.

The observations in the decrease of the mass of the sample with respect to time as the sample got corroded reveal that the corrosion was very fast in the first twenty four hours and almost very very slow after that. This was also true with other concentrations of silver nitrate solution. The surface defects seemed to play a significant role in the corrosion. Thus the rate of corrosion might be considered as a measure of the surface defects. The effective corrosion time parameter was found to be the same independent of the concentration but characteristic of the copper-silver nitrate solution system.

Further work is in progress to investigate this effective corrosion time parameter.

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